

## 2 TREATMENT EFFECTIVENESS

This section presents the results of the demonstration of the E-Beam technology at the NBVC in Port Hueneme, California and describes the effectiveness of the technology in treating groundwater contaminated with MtBE and other gasoline components. The E-Beam technology demonstration was conducted at the Source Zone within the MtBE plume at the NBVC during the Summer and Fall of 2001.

The demonstration at the NBVC was guided by the technical representatives of a group of stakeholders that included the following organizations:

- U.S. EPA, National Risk Management Research Laboratory (NRMRL)
- U.S. Navy, Naval Facilities Engineering Service Center (NFESC)
- U.S. EPA, Region 9
- California Department of Health Services (DHS)

Each of these stakeholders participated in conference calls and meetings at the site to discuss the technical details of the demonstration and to ensure that the technical approach to the demonstration adequately addressed elements of interest to potential users of the E-Beam

technology. NFESC and NRMRL worked cooperatively to staff the field sampling crews and to manage the evaluation.

## 2.1 Background

To characterize the contaminated groundwater at the demonstration location within the Source Zone, seven temporary wells were installed just east of Harris Street in the area of the Extraction Zone. The wells, designated T-1 through T-7, were installed in a line trending north to south with well 1 being the farthest north and well 7 the farthest south. Subsequently, to feed contaminated groundwater to the treatment system, these temporary wells were replaced with a series of five extraction wells, designated S-1 through S-5, as shown in Figure 1-2.

Hydrogeological modeling by NRMRL indicated that the maximum available flow rate from the five extraction wells would be 7 gpm. The E-Beam system was designed for a continuous flow rate of 40 gpm, and Haley and Aldrich indicated that flows lower than about 10 gpm result in some operational difficulties. Therefore, Haley and Aldrich made some refinements to the E-Beam dosing chamber in order to accommodate lower flows and it was planned that the demonstration would be conducted at the maximum available flow rate of 7 gpm.

Groundwater at the Source Zone was known to be contaminated with gasoline components. The primary components of environmental concern included BTEX, MtBE, and products of MtBE degradation, including primarily *t*-butyl alcohol (tBA). To confirm the presence of these components and their approximate concentrations in the area, groundwater samples were collected from the seven temporary wells (T-1 through T-7) in September 2000 and then from the five extraction wells (S-1 through S-5) in March 2001. The results of the laboratory analysis of these groundwater samples are shown in Table 2-1 and confirmed the presence of the expected gasoline components.

In addition to the gasoline components identified above, the stakeholders identified a number of potential by-products of chemical oxidation that may well be formed during treatment of the groundwater using the E-Beam technology. Specifically, by-products from the oxidation of MtBE and BTEX were expected to include acetone, aldehydes, and glyoxals. In addition, bromate formation might result from oxidation of the bromide. Finally, the potential reuse of the effluent as a drinking water supply resulted in the identification of several by-products of subsequent chlorination treatment as constituents of interest. These constituents included total trihalomethanes (TTHM), haloacetic acid (HAAs), and N-nitrosodimethylamine (NDMA).

The contaminants of interest identified above were therefore included on the list of analytical variables to be determined in both influent and effluent samples during the demonstration to assess the effectiveness of E-Beam treatment. Based on a review of regulatory criteria for these contaminants of interest and discussions among the stakeholders, effluent treatment goals were established for selected contaminants of interest as listed in Table 2-2. The treatment goals for MtBE, BTEX and tBA were identified as the lowest maximum contaminant level (MCL) or action level (AL) promulgated by the State of California. For TTHMs and HAAs, the treatment goal was based on the anticipated requirements of the Stage 2 Disinfection By-product Rule (DBPR). These requirements have been proposed in a Notice of Agreement in Principle dated December 20, 2000 (65 FR 251, pages 83015-83024). The other regulatory

criteria presented in Table 2-2 for critical and non-critical variables were used as advisory information and not as a basis for setting the treatment goals for this demonstration.

<b>Table 2-1. Summary of Site Characterization Analytical Results for the Source Zone</b>							
<b>Well No.</b>	<b>Sample ID</b>	<b>MtBE, μg/L</b>	<b>tBA, μg/L</b>	<b>Benzene, μg/L</b>	<b>Toluene, μg/L</b>	<b>Ethylbenzene, μg/L</b>	<b>Xylenes, μg/L</b>
Initial Characterization Sampling Event, September, 2000							
T-1	920	930	NA	400	660	280	1,100
T-2	945	2,600	NA	840	1,100	460	1,600
T-3	1,010	2,200	NA	730*	590	280	950
T-4	1,045	25	NA	233*	110	<1.0	530*
T-5	1,115	6	NA	22	110	370*	870*
T-6	1,530	8	NA	4	17	12	44
T-7	1,555	140	NA	5	26	31	86
Additional Characterization Sampling Event, March 13-14, 2001							
S-1	1,406	569	59	118	<1	7	1,130
S-2	1,440	233	17	0	0	0	3
S-3	1,504	1,400	197	623	276	1,230	1500
S-4	1,535	2,160	270	1,030	<1	470	1500
S-5	1,600	5,100	510	3,170	802	1,740	4030

\*estimated results

NA = not analyzed

**Table 2-2. Development of Treatment Goals for the MtBE Technology Demonstration Program based on Applicable Regulatory Criteria**

Contaminant		CA Primary MCL <sup>a</sup> , µg/L	CA Secondary MCL <sup>a</sup> , µg/L	CA Action Level <sup>a</sup> , µg/L	CA Public Health Goal <sup>a</sup> , µg/L	Stage 2 DBPR MCL <sup>b</sup> , µg/L	Demonstration Treatment Goal, µg/L
VOCs	MtBE*	13	5	NA	13	NA	5
	tBA*	NA	NA	12	NA	NA	12
	Acetone*	NA	NA	NA	NA	NA	NA
	Benzene*	1	NA	NA	0.14 <sup>b</sup>	NA	1
	Toluene*	150	NA	NA	150	NA	150
	Ethylbenzene*	700	NA	NA	300	NA	700
	Xylenes <sup>c</sup> *	1,750	NA	NA	1,800	NA	1,750
DW Variables (SDS Testing)	TTHMs	100	NA	NA	NA	80	80
	HAAs	NA	NA	NA	NA	60	60
	NDMA	NA	NA	0.02	NA	NA	0.02
Aldehydes & Glyoxals	Formaldehyde	NA	NA	NA	NA	NA	NA
	Acetaldehyde	NA	NA	NA	NA	NA	NA
	Heptaldehyde	NA	NA	NA	NA	NA	NA
	Glyoxal	NA	NA	NA	NA	NA	NA
	Me-Glyoxal	NA	NA	NA	NA	NA	NA
Wet Chemistry	Bromate	NA	NA	NA		10	10

**Abbreviations:**

CA: State of California  
 DBPR: Disinfection Byproduct Rule  
 DO: Dissolved Oxygen  
 DW: Drinking Water

EPA: U.S. Environmental Protection Agency  
 HAAs: Haloacetic Acids  
 MtBE: Methyl-t-Butyl Ether  
 NA: Not available  
 SDS: Simulated Distribution System

tBA: t-Butyl Alcohol  
 TBD: To be determined  
 TOC: Total organic carbon  
 TTHMs: Total trihalomethanes  
 VOCs: Volatile organic compounds

**Notes:**

\*: Critical contaminant associated with a primary demonstration objective

- a) Sources: California DHS Primary MCLs and Lead and Copper Action Levels (January 2001), Secondary MCLs (May 2000), Action Levels (February 2001), Public Health Goals (January 2001)
- b) Draft or proposed values
- c) Single isomer or sum of isomers

The demonstration of the E-Beam technology was implemented in two phases. In the first phase, the technology was evaluated during over a two-week period during July 2001 at essentially steady-state operating conditions. For this main phase of the demonstration, a specific set of objectives was formulated and a technology evaluation plan/quality assurance project plan (TEP/QAPP) was written to guide the field sampling, laboratory analysis, and data evaluation efforts. In the second phase, the E-Beam dose was varied in a series of short runs during one week in November, 2001. The purpose of this second phase was to determine the optimum dose for minimizing by-products while still maintaining adequate destruction of the primary contaminants of interest (MtBE and BTEX).

## **2.2 Demonstration Approach: Phase I**

The following sections describe the demonstration objectives and sampling design for Phase 1 of the demonstration, the technology operations during this phase, and the sampling and analytical procedures.

### **2.2.1 Demonstration Objectives and Sampling Design**

One primary objective and six secondary objectives were identified for the main phase of the demonstration. The primary objective and the measurement needed to fulfill this objective were considered critical for the technology evaluation; secondary objectives were related to additional information that was useful but not critical.

#### **2.2.1.1 Primary Objective**

The primary objective was to evaluate whether the E-Beam technology will reduce the MtBE, tBA, and BTEX levels to less than the treatment goals established for the demonstration program. To fulfill this primary objective, grab samples of influent and effluent groundwater were collected three times each weekday for a 2-week period. Each of these samples was analyzed for a list of VOCs that included MtBE, tBA, and BTEX.

#### **2.2.1.2 Secondary Objectives**

The secondary objectives for this demonstration were the following:

1. Monitor for formation of reaction by-products (i.e., acetone, aldehydes, and glyoxals).
2. Determine whether the effluent meets the TTHM and HAAs requirements of the Stage 2 DBPR when subjected to Uniform Formation Conditions (UFC).
3. Use a chloramine UFC test to assess potential for formation of NDMA.
4. Monitor certain water quality variables, including pH, temperature, dissolved oxygen (DO), chemical oxygen demand (COD), and dissolved and total organic carbon (DOC/TOC), as well as the flow rate.
5. Define operating costs (power/energy consumption, chemical costs) over a set period of stable operation.

6. Determine if the technology results in a significant increase in the bromate concentration in the effluent as compared to the influent.

To fulfill Secondary Objectives 1, 4, and 6, grab samples of the influent and effluent groundwater were collected once each weekday and analyzed for the listed variables. To fulfill Secondary Objectives 2 and 3, grab samples of the effluent were collected two times during the demonstration and shipped to the NRMRL drinking water laboratory, where the samples were subjected to chlorination according to Simulated Disinfection System (SDS) testing protocols.

### **2.2.2 Technology Operations**

The pump and hosing that was already present in the pump room of the E-Beam process trailer was used to extract groundwater from the five extraction wells into the E-Beam treatment system. The flow from the wells was fed directly into the treatment system, bypassing the influent tank, and the effluent was discharged to the NBVC sanitary sewer system under an appropriate permit. To determine the hydraulic residence time of the treatment system, a tracer study was conducted following startup of the E-Beam system but prior to initiation of the treatment runs. Sodium chloride was added to the influent and the effluent was monitored with a conductivity meter to determine the mean residence time. The test was repeated four times at the planned flow rate of 7.0 gpm; the mean hydraulic residence time was calculated to be 2 minutes and 45 seconds.

During Phase 1, the E-Beam system was operated at a power input corresponding to a radiation dose of 1,200 krads, which Haley and Aldrich indicated would be adequate to destroy MtBE at the concentrations historically observed at this location. The E-Beam treatment system was operated only during the day, from approximately 7 a.m. to 6 p.m., and was shut down at night at the request of the NBVC for security and safety reasons. Each morning during the demonstration period, the system was started up by the E-Beam operator and allowed to run for approximately 1 hour to ensure that the process was at a steady operational state before any sampling was conducted.

### **2.2.3 Sampling and Analytical Procedures**

During the demonstration, grab samples of the groundwater were collected before and after treatment at the E-Beam influent and effluent sampling locations. Sampling was conducted between the hours of 8 a.m. and 6 p.m. each day. Three grab samples were collected for volatile organic compound (VOC) analysis at about 4-hour intervals on each of the 10 sampling days to generate a total of 30 samples for VOCs. One grab sample was collected each sampling day for analysis of aldehydes/glyoxals and general water quality characteristics to generate a total of 10 samples for each of these variables.

All samples were collected directly into sample jars from the valved taps in the E-Beam system influent and effluent lines. Prior to sample collection, the valved water taps were purged briefly to ensure that any stagnant water had been flushed out of the tap. A description of the sample container and preservative utilized for each type of sample is provided in Table 2-3. Each water sample for VOC analysis was collected in three 40-mL volatile organic analysis (VOA) vials containing hydrochloric acid to acidify the sample to a pH < 2. The water sample was gently introduced into the sample containers to reduce agitation and loss of volatile compounds.

Each vial was filled until a meniscus appeared over the top of the vial. The screw-top lid with the septum (Teflon side toward the sample) was then tightened onto the vial. After the lid was tightened, the vial was inverted and tapped to check for air bubbles. If any air bubbles were present, the sample was recollected. For all other analytes, water was introduced directly into the appropriate container, as listed in Table 2-3, and the lid was tightened immediately after filling. Field duplicates and other quality control (QC) samples were collected immediately following collection of the original sample. After collection, each water sample was stored on ice in a cooler until readied for shipment to the analytical laboratory. All sample collection procedures were in accordance with the reference method listed in Table 2-3.

To evaluate the potential formation of by-products after treatment with the electron beam process, it was determined that the SDS testing protocol, which was established under the DBPR and simulates the effects of chlorination under UFC, would be used. A bulk 1-gallon effluent water sample, before and after treatment, was collected two times during the demonstration and sent to NRMRL for SDS testing and subsequent analysis of chlorination by-products.

Following sample collection, each sample was labeled with detailed information regarding the location, date, and time of collection. Chain-of-custody procedures were followed from sample collection through sample analysis.

Each effluent grab sample was taken approximately one hydraulic retention time following the collection of the corresponding influent sample to ensure that the same parcel of water was being sampled before and after treatment. Since the flow rate was maintained at 7.0 gpm throughout the demonstration, effluent samples were taken about 2 minutes and 45 seconds following collection of the influent sample during each sampling event.

Field variables that were measured on influent and effluent water included pH, temperature, and DO. These measurements were taken using a Horiba U-22 water quality meter on a separate grab sample in conjunction with each influent/effluent sampling event. Laboratory measurements that were conducted are listed in Table 2-3. All laboratory measurements were conducted in accordance with the EPA reference method.

## **2.3 DEMONSTRATION APPROACH: PHASE 2**

During Phase 2, the E-Beam system was operated at three different power inputs, corresponding to radiation doses of 800, 1,200, and 1,600 krad. The flow rate and other operating conditions for Phase 2 were the same as for Phase 1. Because influent groundwater was pumped directly from the extraction wells, and these wells had only recently been installed, there was some concern that the influent groundwater might contain atypically high levels of suspended matter. To assess whether this suspended matter might have any influence on the performance of the treatment system, a replicate run was conducted at each of the three power levels wherein a 1-micron cartridge filter was inserted into the influent line to filter out suspended matter prior to treatment. The sampling and analytical procedures for Phase 2 of the demonstration were identical to Phase 1.

## **2.4 RESULTS FOR PHASE 1**

All planned measurements were taken, and no outliers were identified. Thus, 100% completeness was achieved for field variables. The results are summarized below:

- The flow rate ranged from 6.8 to 7.0 gpm, and averaged 6.97 gpm.
- The pH averaged 6.80 in the influent and 7.01 in the effluent.
- The dissolved oxygen content of the groundwater increased from 5.70 mg/L in the influent to 7.32 mg/L in the effluent.
- The temperature of the influent averaged 23.9° C; the effluent temperature averaged about 26.2°C (2.3° C higher).



Table 2-3. Analytical Variables and Method Requirements						
Analytical Variable	Target Analytes	Method Reference	Container	Holding Time	Preservation	Analytical Laboratory
Volatile organics	MtBE	SW-846 5030B/8260B	3 x 40 mL amber glass vial	1-4 days (anal.)	HCl to pH<2	ALSI
	tBA					
	BTEX					
	Acetone					
Aldehydes/Glyoxals	Formaldehyde	MDOCDW 556 Mod.	2 x 50 mL amber glass	7 days(ext)/ 14 days (anal)	25 mg CuSO <sub>4</sub> .5H <sub>2</sub> O	MW
	Acetaldehyde					
	Methyl glyoxal					
	Glyoxal					
	Heptaldehyde					
General Chemistry	TOC	MCAWW 415.1	1 x 250 amber glass	28 days	HCl to pH<2	ALSI
	DOC	MCAWW 415.1 Mod.			H <sub>2</sub> SO <sub>4</sub> to pH<2	
	COD	MCAWW 410.4			None	
	Bromide ion	MCAWW 300.0	1 x 500 mL polyethylene		5 mg EDA	MW
	Bromate ion	MCAWW 317	1 x 50 mL amber glass			
Bulk SDS Test Sample	NA	SDS UFC Test	6 x 1 L amber glass	Not specified	None	EPA NRMRL
Disinfection Byproducts (in SDS Effluent)	TTHMs	MDOCDW 551	2 x 60 mL amber glass	14 days (ext)/ 14 days (anal)	10 mg NH <sub>4</sub> Cl	
	HAAs	MDOCDW 552.1	2 x 50 mL amber glass	14 days (ext)/ 7 days (anal)		
		NDMA	40 CFR 136, Meth. 1625 Mod.	2 x 1 L amber glass	30 days (ext/ anal)	20 mg ascorbic acid

Abbreviations:

ALSI: Analytical Laboratory Services, Inc

Anal: Analysis

CFR: Code of Federal Regulations

COD: Chemical Oxygen Demand

CuSO<sub>4</sub>.5H<sub>2</sub>O: Copper sulfate pentahydrate

DOC: Dissolved Organic Carbon

EDA: Ethylene diamine

Ext.: extraction

HAAs: Haloacetic acids

MCAWW: Methods for the Chemical Analysis of Water and Wastes (EPA 1998a)

MDOCDW: Methods for determination of organic compounds in drinking water

MW: Montgomery Watson Laboratories

NDMA: N-nitrosodimethylamine

NRMRL: National Risk Management Research Laboratory

SDS: Simulated Distribution System

SW-846: Test Methods for the Evaluation of Solid Wastes (EPA 1996)

TOC: Total organic carbon

TFE: tetrafluoroethene

TTHMs: total trihalomethanes

UFC: Uniform Formation Conditions

The increase in effluent temperature was consistent with the process chemistry for the E-Beam technology, as discussed in Section 1.3.1. A 100% completeness was achieved for laboratory variables with the exception of NDMA. Other analytical tests consumed the entire available SDS effluent sample; therefore, insufficient sample was available to the laboratory for NDMA analysis.

#### 2.4.1 Trends in Results for Critical VOCs

The laboratory analytical results for each critical VOC variable are plotted in Figure 2-1 and 2-2. In each of these plots, the date of sampling is shown on the x-axis, and the concentrations of the critical variables are shown on the y-axis.

Figure 2-1 shows the influent and effluent MtBE (upper panel) and tBA (lower panel) concentrations during the two-week demonstration period. Each day, 3 replicate samples were collected, one in the morning, one around noon to mid-afternoon, and one in late afternoon. The effluent samples were temporally related to the influent samples. Since the scale of the figure is logarithmic, the increase in influent MtBE concentration from 1,400 to 2,000 over the time period is not clearly noticeable. This increasing trend in influent MtBE concentration may have resulted from the drawing in of higher concentration regions of the plume into the extraction wells. Effluent MtBE concentrations were always less than the treatment goal of 5 µg/L established at the beginning of the project (dotted horizontal line in the figure), and variability was low.

The lower panel of Figure 2-1 summarizes the influent and effluent tBA concentrations. The dotted horizontal line signifies the treatment goal of 12 µg/L, which was the compliance target established in the project objectives. tBA was never in compliance with that treatment goal for the duration of the demonstration period at the dose rate studied. The rate constant for the reaction of hydroxyl radical with tBA is  $6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , or about half that of MtBE. Therefore, even though MtBE removal was consistently effective, tBA removal was consistently less so. This is because of the competition for high energy electrons and oxidative radicals by the other organic constituents in the influent groundwater as well as the lower rate constant for oxidation of tBA as compared to other organic constituents.

Figure 2-2 (a-d) summarizes the behavior of the BTEX compounds in the groundwater during the 2-week demonstration period. Again, the dotted lines in the figure panels represent the treatment goals for the respective compounds. Benzene and toluene were both consistently reduced by 3 orders of magnitude to below their respective treatment goals. Ethylbenzene and xylenes were already below their treatment goals in the influent, and they were reduced further to below detection limits by exposure to the electron beam (the laboratory quantitation limit was 0.5 µg/L for ethylbenzene and 1.5 µg/L for total xylenes).

Figure 2-1. MtBE and tBA Influent and Effluent Concentrations over the Phase 1 Demonstration Period

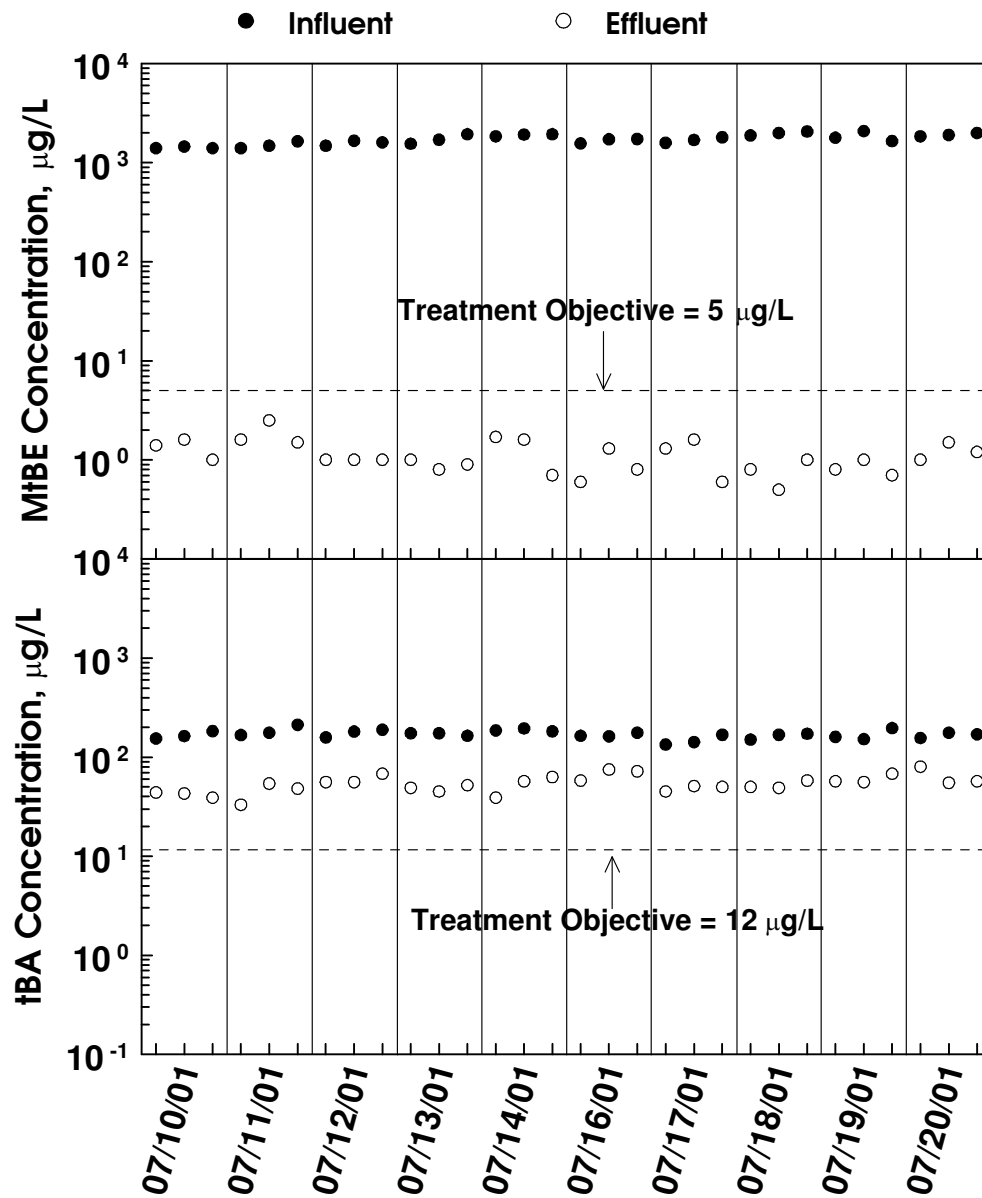
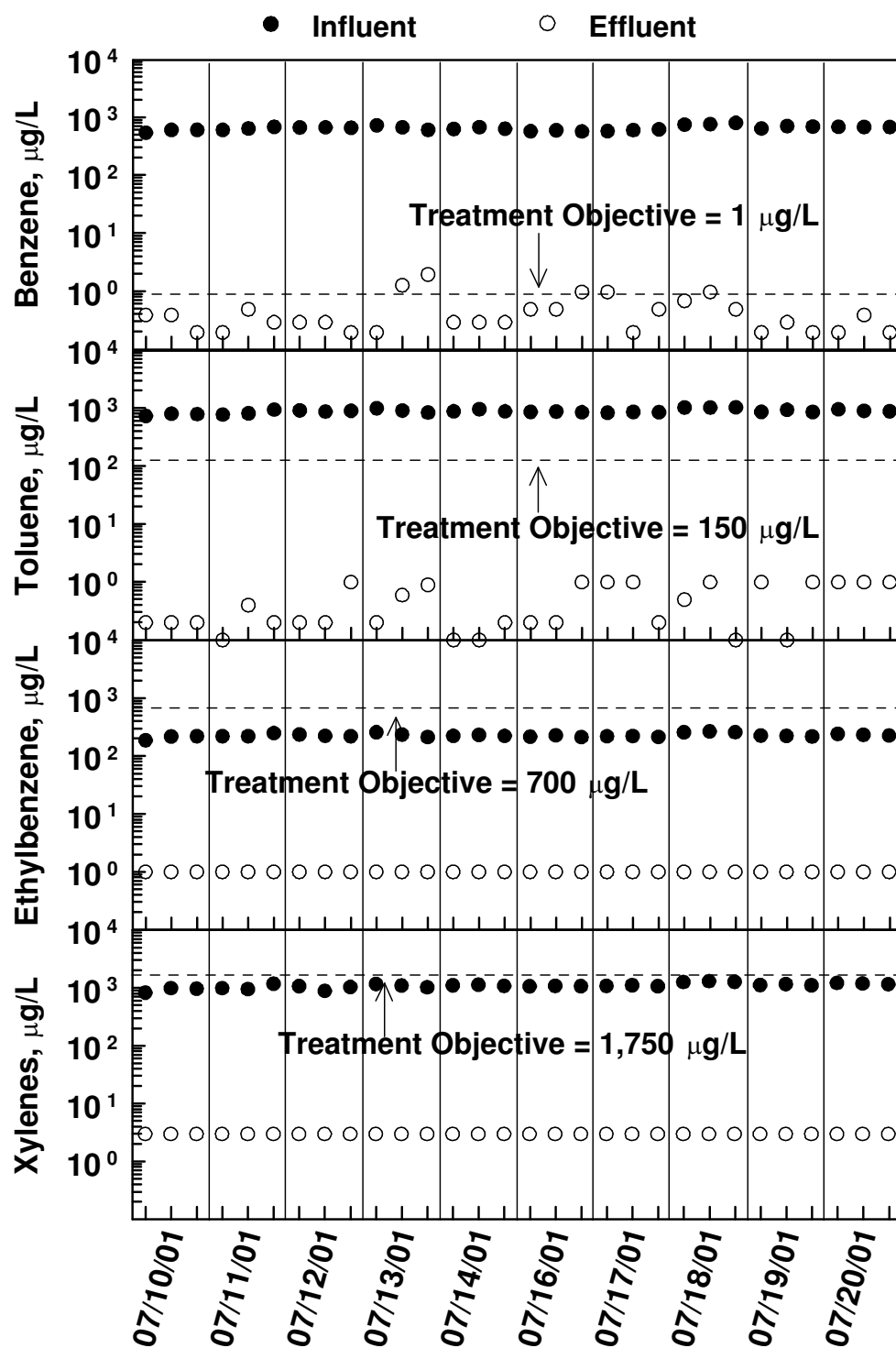


Figure 2-2. BTEX Influent and Effluent Concentrations over the Phase 1 Demonstration Period



## 2.4.2 Statistical Analysis of Results

In accordance with the TEP/QAPP, a preliminary statistical evaluation of the laboratory analytical results for each measured target analyte was conducted. Descriptive summary statistics were calculated for each contaminant of interest in the influent and effluent groundwater. To calculate these statistics, non-detections were replaced with a simple substitution of one-half the laboratory quantitation limit. Statistical plots were generated to graphically describe the concentrations of these contaminants in the sample populations of influent and effluent water.

Normal probability plots depicting the data for MtBE, tBA, and BTEX showed a reasonable fit to a theoretical normal distribution for most of these variables. Two contaminants (ethylbenzene and xylenes) were not detected in any effluent samples, so statistical tests were not applicable. For each of the other four variables, a normal distribution was assumed and the one-sample, one-tailed t-distribution was used to calculate 95 percent confidence limits and to perform statistical comparisons to the treatment goal.

The critical contaminants that were established to be tested for compliance with treatment goals in the project objectives included MtBE, tBA, and BTEX. Table 2-4 lists the mean and the 95 percent upper confidence limit (UCL) of the mean influent and effluent concentrations of these contaminants, as well as the overall removal efficiency. Figures 2-3 and 2-4 compare the mean influent and daily UCL for the effluent concentrations of these contaminants to the treatment goals. As shown in Figure 2-3, the daily effluent UCL for MtBE was consistently below the 5- $\mu\text{g/L}$  treatment goal. However, for tBA, the daily effluent UCL was significantly above the 12  $\mu\text{g/L}$  treatment goal. In all cases except tBA and one point for benzene, the effluent concentrations of these critical contaminants were in compliance with project objectives. As stated in Section 2.4.1, the rate constant for reaction of hydroxyl radicals with tBA is about half that for MtBE. Thus, the presence of other organic compounds in the groundwater competing for the hydroxyl radicals and aqueous electrons would have a greater influence on tBA destruction than MtBE.

Table 2-5 and Figure 2-5 present the performance of the electron beam in regards to its effect on the measured oxidation by-products (acetone, formaldehyde, glyoxal, and bromate ion). Table 2-5 lists the mean and the overall 95 percent upper confidence limit (UCL) of the mean influent and effluent concentrations of these contaminants. Figure 2-5 compares the daily influent and effluent concentrations of these contaminants over the time period of Phase 1 of the demonstration. All of the organic by-products increased substantially in concentration from the influent to the effluent as a result of chemical oxidation reactions. Acetone and formaldehyde were the two most prevalent organic by-products, which is consistent with results of previous studies of chemical oxidation processes in similar applications. Bromate ion did not increase in concentration from the influent to the effluent and was present only at concentrations near the laboratory quantitation limit (1.0  $\mu\text{g/L}$ ) in both these streams.

**Table 2-4. Mean, 95 Percent UCL, and Removal Efficiency for MtBE, tBA, and BTEX**

Compound	Influent		Effluent		Removal Efficiency
	Mean Concentration, $\mu\text{g/L}$	UCL, $\mu\text{g/L}$	Mean Concentration, $\mu\text{g/L}$ <sup>1</sup>	UCL, $\mu\text{g/L}$ <sup>1</sup>	
MtBE	1721	1784.5	1.1	1.2	99.94%
tBA	170	175.3	54.2	57.6	68.14%
Benzene	664	683.1	0.4	0.6	99.94%
Toluene	890	913.3	0.3	0.4	99.97%
Ethylbenzene	220	233.5	ND(0.5)	NA	>99.77%
Total Xylenes	1090	1123.7	ND(1.5)	NA	>99.86%

<sup>1</sup> Where less than 20 percent non-detects were present in the sample population, the mean concentration and UCL were determined by setting non-detect results equal to one-half the laboratory quantitation limit.

NA = Not applicable; a UCL could not be calculated because most results were non-detects.

ND = Not detected in any of the effluent samples.

UCL = 95 percent upper confidence limit for the mean

**Table 2-5. Concentrations of By-products in Influent and Effluent Water**

Compound	Influent		Effluent	
	Mean Concentration, $\mu\text{g/L}$ <sup>1</sup>	UCL, $\mu\text{g/L}$ <sup>1,2</sup>	Mean Concentration, $\mu\text{g/L}$	UCL, $\mu\text{g/L}$ <sup>2</sup>
Acetone	6.9	8.8	160	165.0
Acetaldehyde	1.1	1.3	14.7	15.7
Formaldehyde	6.8	7.3	125.0	136.0
Glyoxal	1.7	2.0	8.8	10.5
M-Glyoxal	1.2	1.5	34.5	37.4
Bromate	1.3	1.6	1.3	1.6

<sup>1</sup> Where non-detects were present in the sample population, the mean concentration and UCL were determined by setting non-detect results equal to one-half the laboratory quantitation limit.

<sup>2</sup> The UCL listed reflects a one-sided 95 percent probability upper limit for the population mean using a t-test.

UCL = Upper confidence limit

Figure 2-3. Mean Influent and 95 Percent UCL Effluent Concentrations of MtBE and tBA in the Phase I Portion of the Demonstration.

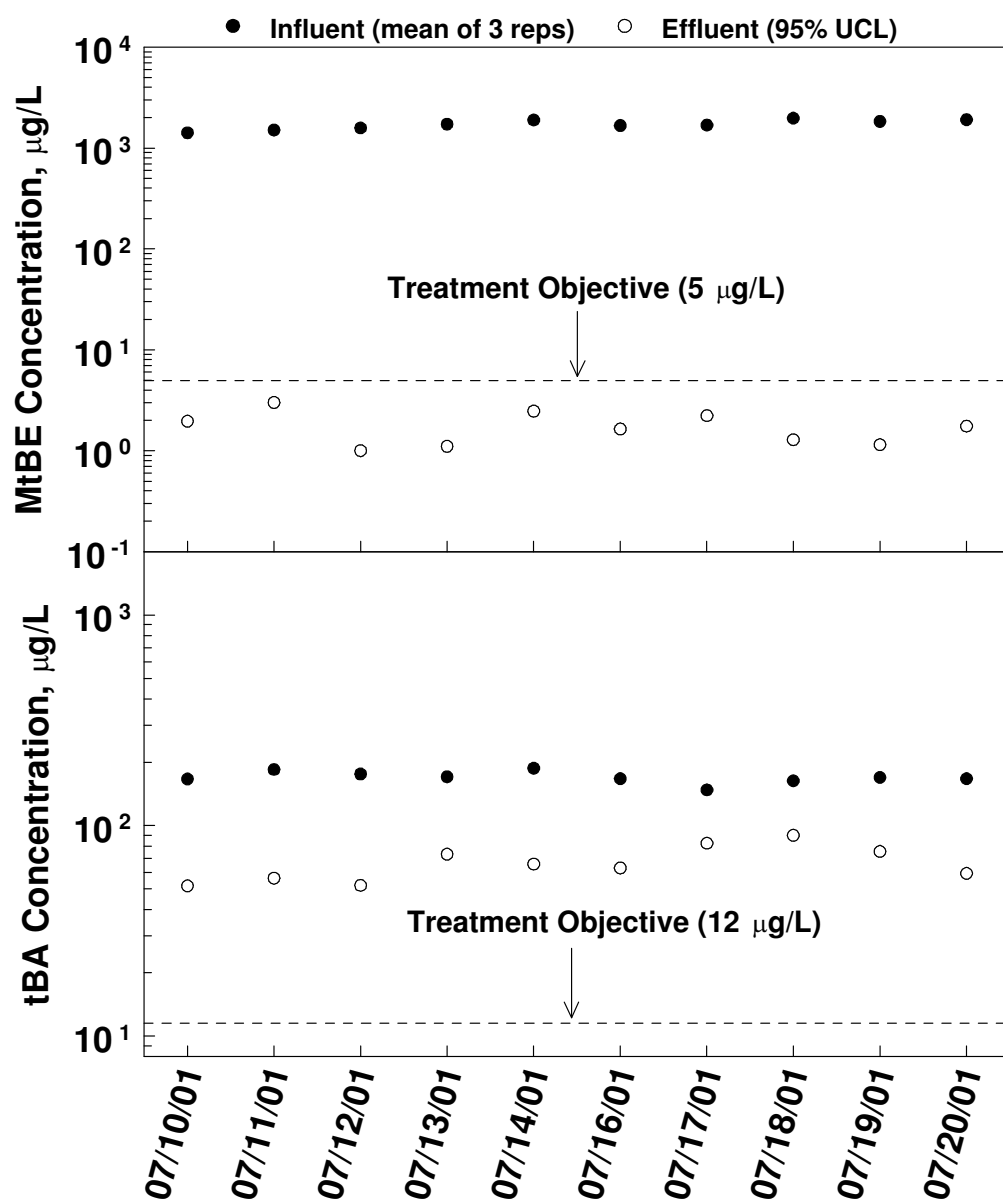


Figure 2-4. Mean Influent and 95 Percent UCL Effluent Concentrations of BTEX in the Phase I Portion of the Demonstration.

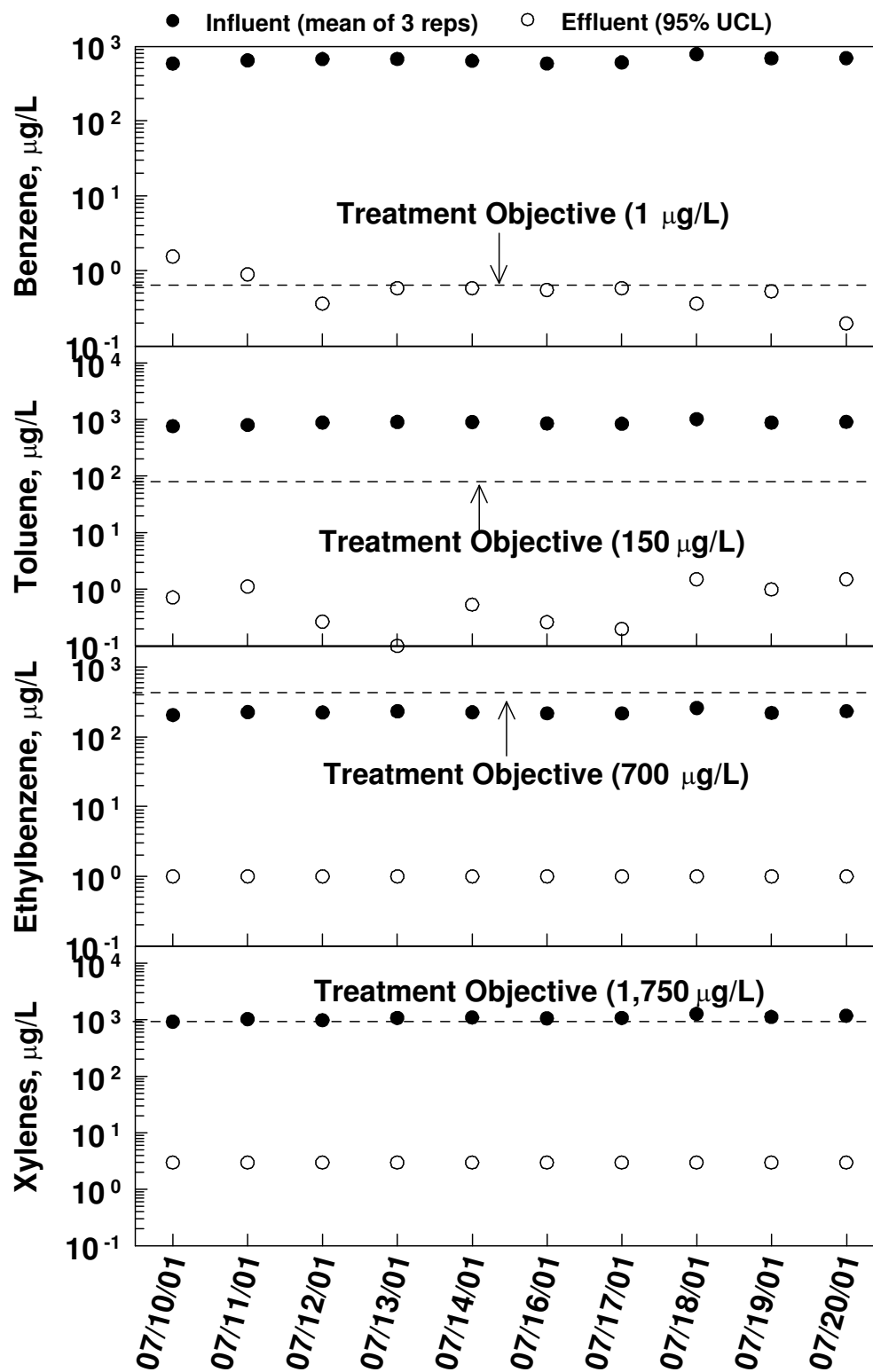




Figure 2-5. Acetone, Formaldehyde, Glyoxal, and Bromate Influent and Effluent Concentrations in the Phase 1 Portion of the Demonstration (the square symbols in the bottom panel represent the fact that the bromate concentrations in the influent and effluent were identical).

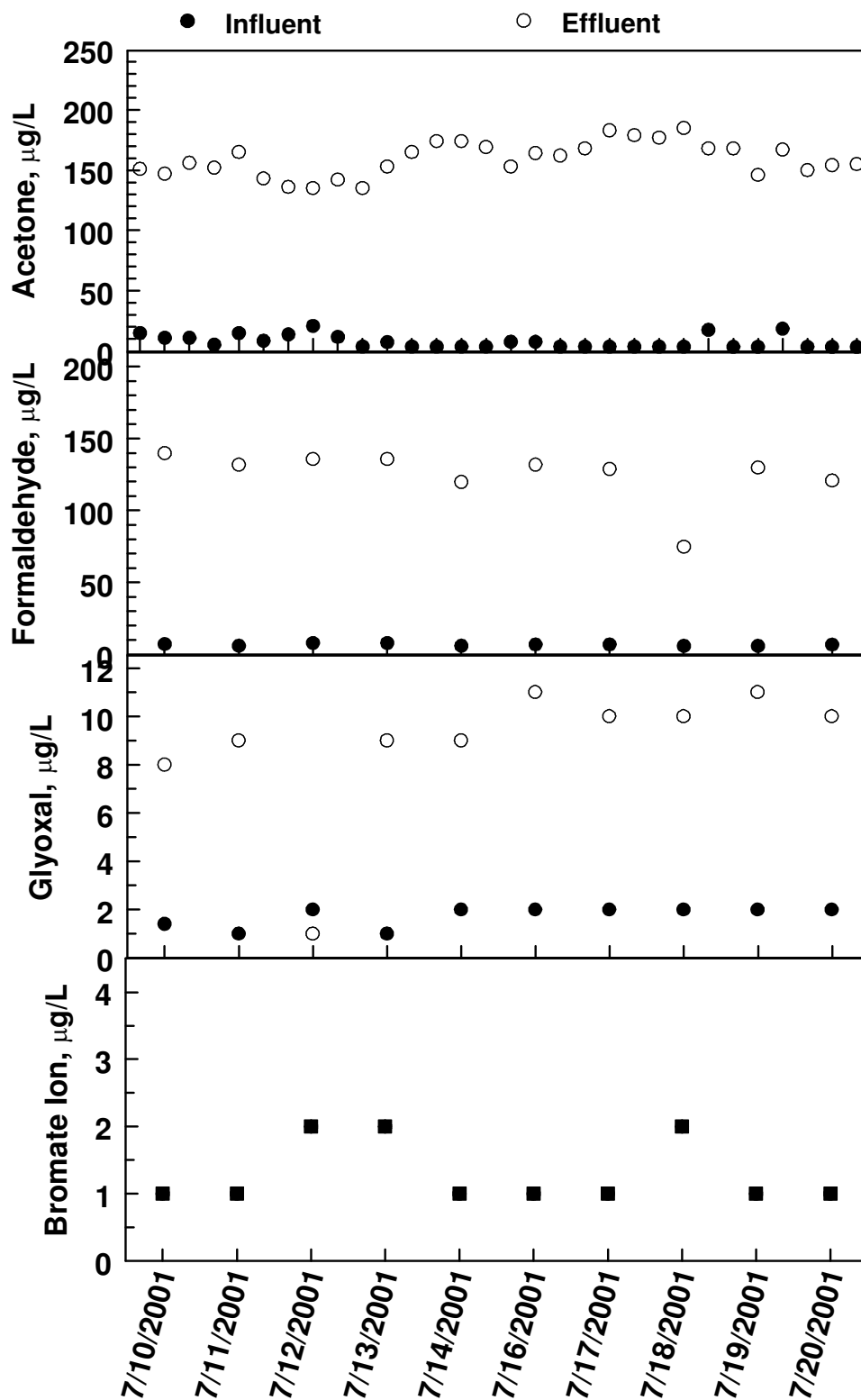


Table 2-6 and Figure 2-6 show the effect of the electron beam on other measured water quality variables (COD, TOC, DOC, and bromide ion). Table 2-6 lists the mean and the UCL for influent and effluent concentrations of these analytical variables. Figure 2-6 compares the daily influent and effluent concentrations of these variables over the time period of Phase 1 of the demonstration. COD concentrations were nearly identical in the influent and effluent streams, but both TOC and DOC increased significantly in concentration from the influent to the effluent. Bromide ion concentration did not change in response to exposure to the E-Beam.

**Table 2-6. Concentrations of General Water Quality Variables in Influent and Effluent Water**

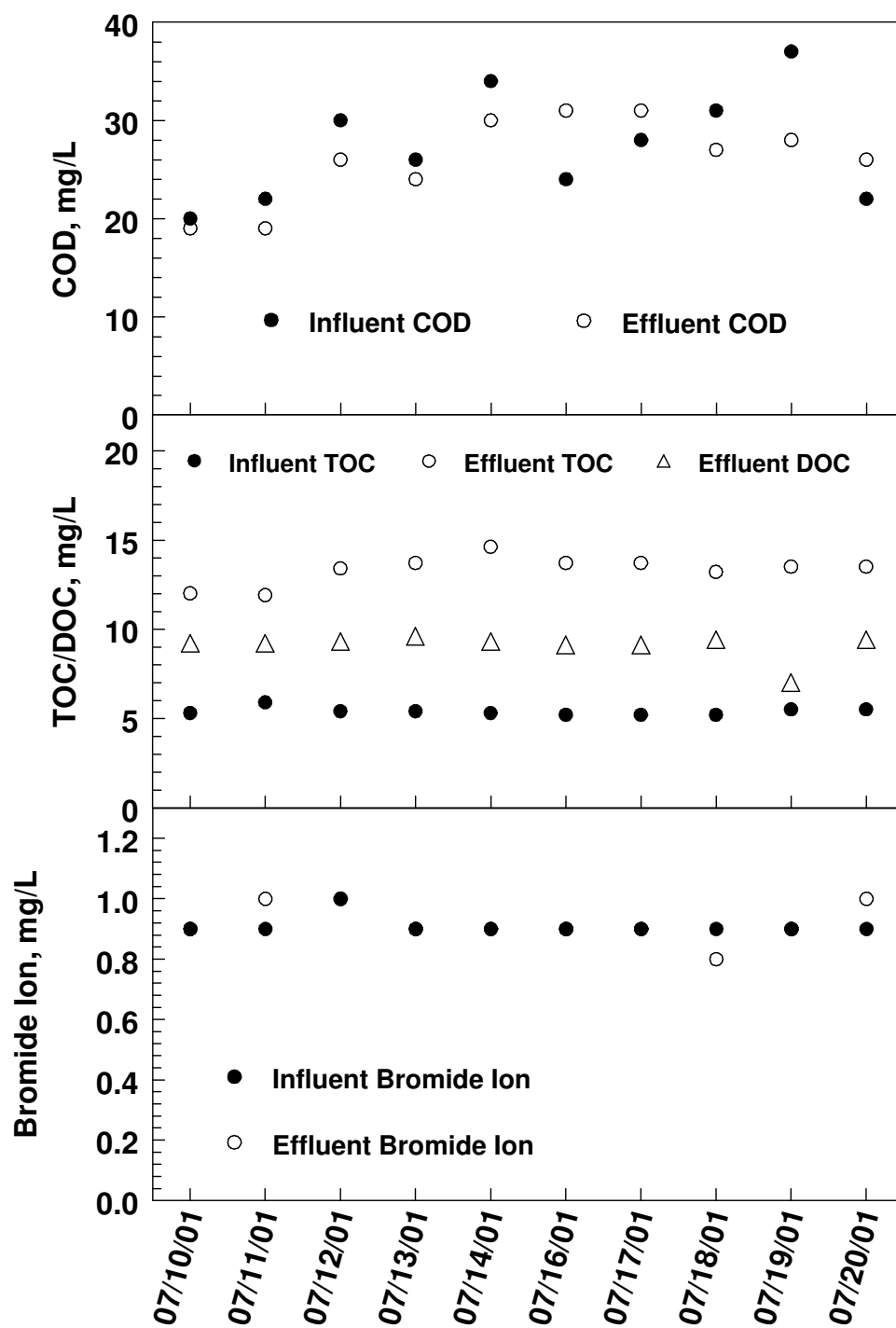
Compound	Influent		Effluent	
	Mean Concentration mg/L <sup>1</sup>	UCL, mg/L <sup>1, 2</sup>	Mean Concentration mg/L <sup>1</sup>	UCL, mg/L <sup>1, 2</sup>
TOC	5.4	5.5	13.3	13.8
DOC	5.0	5.2	9.1	9.5
COD	27.4	30.6	26.1	28.6
Bromide	0.9	0.9	0.9	1.0

<sup>1</sup> Where non-detects were present in the sample population, the mean concentration and UCL were determined by setting non-detect results equal to one-half the laboratory quantitation limit.

<sup>2</sup> The UCL listed reflects a one-sided 95 percent probability upper limit for the population mean using a t-test.

UCL = Upper confidence limit

Figure 2-6. COD, TOC/DOC, and Bromide Ion Influent and Effluent Concentrations Over the Phase 1 Demonstration Period.



### 2.4.3. Evaluation of Results Against the Objectives

This section assesses the results of Phase 1 of the E-Beam demonstration in relation to the stated primary and secondary objectives.

Primary Objective: Does the technology reduce the final levels of MtBE, tBA, and BTEX to less than the treatment goals established for the demonstration program? The primary objective was addressed by comparing the UCL for the effluent concentrations of MtBE, tBA, and BTEX to the treatment goals. As described previously, the UCLs were calculated at the 95% confidence level for the means using the one-tailed t-distribution. The overall average UCL for the mean concentrations of MtBE (1.2 µg/L), benzene (0.6 µg/L), and toluene (0.4 µg/L) in the effluent were below the corresponding treatment goals of 5 µg/L, 1 µg/L, and 150 µg/L, respectively. As a result, it was concluded that the primary objective was met for these compounds. The UCL for the mean concentration of ethylbenzene and of total xylenes in the effluent water could not be calculated because all concentrations for these contaminants were below the laboratory quantitation limit. However, the laboratory quantitation limit was less than the treatment goal for each variable; therefore, it was concluded that the primary objective was met for these contaminants as well. In fact, the influent concentrations were already less than the treatment goals.

The UCL for the mean concentration of tBA in effluent water was 57.6 µg/L, which was well above the treatment goal of 12 µg/L. Because the treatment goal was not achieved for tBA, the primary objective for tBA was not met.

Secondary Objective No. 1: Monitor for formation of undesirable reaction by-products, such as acetone, aldehydes, and glyoxals. Other studies of the E-Beam technology and of chemical oxidation processes suggest that partially oxidized organic compounds such as acetone, aldehydes, and glyoxals may result from incomplete oxidation of VOCs and may remain in the effluent from the process (EPA, 1997). This finding was confirmed in the results of the E-Beam technology demonstration at the NBVC. As shown in Table 2-5, concentrations of acetone, acetaldehyde, formaldehyde, glyoxal, and methyl glyoxal in effluent samples were many times the concentrations measured in influent samples, indicating that these compounds were formed during the E-Beam treatment.

There did not appear to be any trends in the concentrations of partially oxidized organic by-products over the two-week demonstration period even though influent organic contaminant concentrations did exhibit increasing trends as described previously. Thus, results indicate that by-product formation was not directly related to influent organic contaminant concentrations.

Secondary Objective No. 2: Determine whether the effluent meets the TTHM and HAA requirements of the Stage 2 DBPR when subjected to UFC. To compare the effluent concentrations with the TTHM and HAA requirements of the Stage 2 DBPR, two influent samples and two effluent samples were subjected to SDS testing. These samples were chlorinated according to UFC protocols and analyzed for TTHM and HAAs. The analytical results of these samples indicated that TTHM and HAAs were formed at levels exceeding the Stage 2 DBPR criteria in both the influent and the effluent samples (see Table 2-7). However, concentrations of TTHM and HAAs were significantly elevated in the effluent samples that were

processed, indicating that the E-Beam treatment generated precursors to the formation of TTHMs and HAAs.

One possible source of the TTHMs was the acetone produced from reaction of the hydroxyl radical with MtBE. Hypothetically, assuming one mole of acetone gives rise to one mole of chloroform (the iodoform reaction), then the mean 160 µg/L acetone (2.78 µM) (Table 2-5) would give rise to 321 µg/L of chloroform. Although this does not account for the total increase in TTHM formation, it is one plausible pathway that could partially explain the increase observed.

Secondary Objective No. 3: Use a chloramine UFC test to assess potential for formation of NDMA. As stated above, insufficient sample was available following SDS testing to complete the NDMA analysis. Thus, no results were obtained for NDMA.

Secondary Objective No. 4: Monitor certain water quality variables, including pH, temperature, DO, COD, and DOC and TOC, as well as the flow rate through the system. During the treatment demonstration, the field team measured the flow, pH, temperature, and DO of influent and effluent water at the sampling locations during each of the three daily sampling events. The results of these measurements were summarized in Sections 2.4 and 2.4.2.

**Table 2-7. Summary of TTHM and HAA Results**

Compound	Influent Concentration, µg/L	Effluent Concentration, µg/L	Stage 2 DBPR MCL, µg/L
TTHM	165.8	841.4	80
	195.6	631.9	
HAAs	168.7	682.6	60
	169.7	628.3	

Secondary Objective No. 5: Define operating costs (energy consumption, chemical costs) over a 2-week period of stable operation. Operating costs are discussed in the economic analysis of the E-Beam technology in Section 3. The economic analysis utilized operating data from previous demonstrations as well as information collected during this demonstration.

Secondary Objective No. 6: Determine if the technology results in a significant increase in the bromate ion concentration in the effluent as compared to the influent. Table 2-5 lists the mean, as well as the 95% UCL of the mean for bromate ion in both the influent and effluent. These results show that the concentration of bromate ion did not increase from the influent to the effluent. This result was not unexpected since the literature has shown that the E-Beam process is effective in reducing bromate ion to bromide ion (Siddiqui et al., 1996a; 1996b).

## 2.5 RESULTS FOR PHASE 2

All planned measurements were taken, and no outliers were identified. Thus, 100% completeness was achieved for field variables. The results for field variables are summarized below:

- The influent flow rate ranged from 6.8 to 7.3 gpm, and averaged 7.04 gpm, during the two days of the Phase 2 testing
- The pH averaged 7.04 in the influent and 7.07 in the effluent.
- The dissolved oxygen content of the groundwater increased from 4.1 mg/L in the influent to 5.3 mg/L in the effluent.
- The temperature of the influent averaged 22.0°C; the effluent temperature averaged about 2.0°C higher at 24.0°C.
- Turbidity averaged 1.03 NTU in the influent water.

Concentrations of MtBE and tBA in the effluent (both filtered and unfiltered) declined with increasing dose, as shown in Figure 2-7. A dose of 800 krads was not quite sufficient to reduce the concentration of MtBE to below the treatment goal of 5.0 µg/L, but higher doses were effective in meeting this treatment goal. tBA (unfiltered) was not consistently reduced to below the treatment goal of 12 µg/L even at the highest dose (1,600 krads). However, the trend shown in Figure 2-7 indicates that tBA could have been reduced to below the treatment goal of 12 µg/L at a dose of about 2,000 krads.

Results for BTEX compounds (Figure 2-8) consisted largely of non-detects even at the lowest dose (800 krad). Therefore, there was no measurable difference in performance for BTEX compounds in the power range tested.

Figure 2-7. Concentrations of MtBE and tBA in Filtered and Unfiltered Groundwater as a Function of Applied E-Beam Dose.

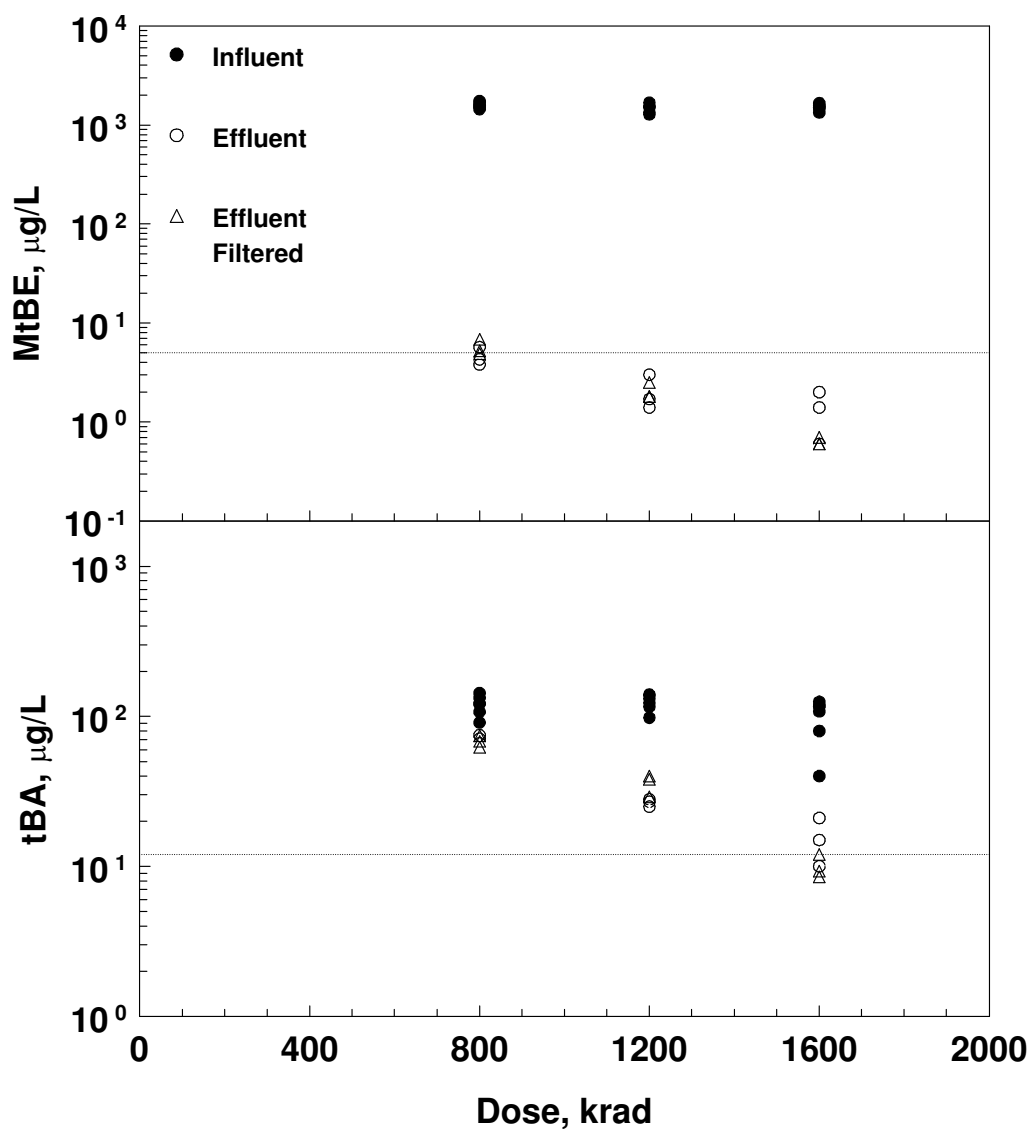
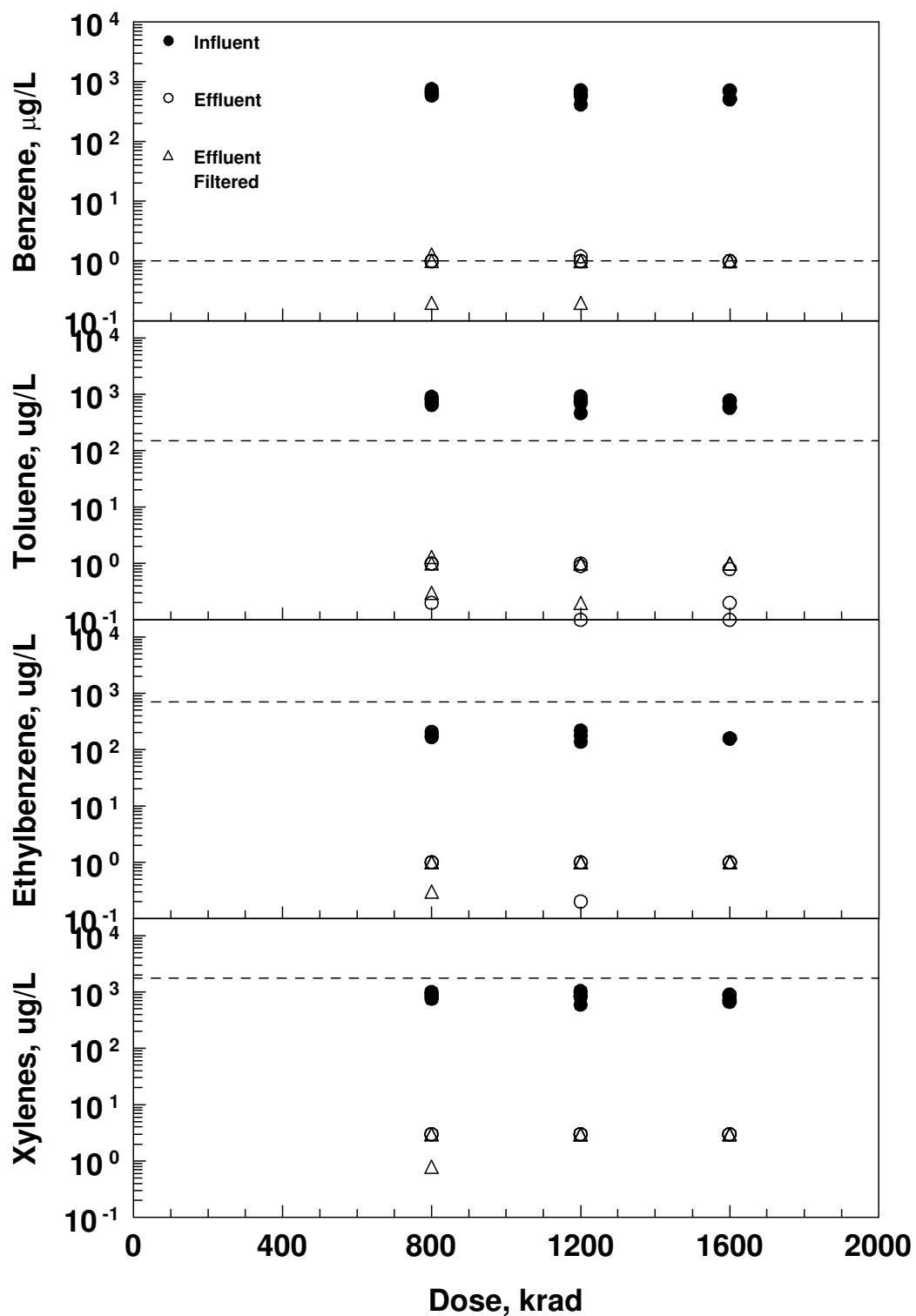


Figure 2-8. Concentrations of BTEX in Filtered and Unfiltered Groundwater as a Function of Applied E-Beam Dose.





## 2.6 QUALITY ASSURANCE AND QUALITY CONTROL RESULTS

A data quality review was conducted by Tetra Tech to evaluate the field and laboratory QC results, evaluate the implications of QC data on the overall data quality, document data use limitations for data users, and remove unusable values from the demonstration data sets. The results of this review were used to produce the final data sets to assess the treatment technology and to draw conclusions. The QC data were evaluated with respect to the quality assurance (QA) objectives defined in the project QAPP (Tetra Tech, 2001).

The analytical data for the groundwater samples collected during the E-Beam demonstration were reviewed to ensure that they are scientifically valid, defensible, and comparable. A data quality review was conducted using both field QC samples and laboratory QC samples. The field QC samples included source water blanks, field blanks, trip blanks, matrix spike/matrix spike duplicates (MS/MSD), and sample duplicates. Laboratory QC checks included laboratory blanks, surrogate spikes, and laboratory control sample/laboratory control sample duplicates (LCS/LCSD) (also known as blank spike/blank spike duplicates). Initial and continuing calibration results were also reviewed to ensure the quality of the data and that proper procedures were used. The review focused on assessing the precision, accuracy, completeness, representativeness, and comparability of the data.

All critical variable data were reviewed and at least one sample from each phase of the demonstration was fully validated (recalculated from the raw instrument data). In addition to the above QC checks, reviews of sample chain of custody, holding times, and critical variable identification and quantification were performed.

Overall, the data quality review assessed the critical variable data to be useable for the purpose of evaluating the technology and the attainment of the primary objective for this demonstration. In some instances, results for one or more QC variables were outside of control limits; however, deviations were generally slight, and no broad qualifications of data or other actions were required. A description of the more significant deviations from QC acceptance criteria and the limited impact of these deviations are described below:

- Continuing calibration criteria (percent difference values, or %D) exceeded QAPP criteria for tBA in a few instrument calibration checks during the Phase 2 sampling event. These exceedances were slight, however, and no data were rejected due to calibration problems.
- MtBE was detected at concentrations below 0.4 µg/L in all but one of the method blanks associated with the Phase 2 sampling event. MtBE was detected at similar concentrations in 4 of the 5 trip blanks from this event. Based on laboratory audit findings, these detections are apparently due to the presence of MtBE in the well water used to prepare the blanks. Thus, these blank results were assessed not to indicate a potential high bias in low concentrations of MtBE measured in demonstration effluent samples collected during the Phase 2 sampling event.
- Low concentrations of toluene and other BTEX compounds were detected on an isolated basis in method blanks and trip blanks. As a result, a few low-level results

reported in demonstration effluent samples at less than 5 times associated blank detections were qualified as not detected in the final demonstration data set.

- For the VOC analyses, MS and MSD percent recoveries were generally within the acceptance criteria of 75 to 125% with only a few exceptions, and no data were rendered unusable due to MS/MSD results. In some cases, the percent recoveries for MtBE and other critical variables were above the QC limits in MS/MSDs performed on influent water samples. However, these recoveries were affected by the high native concentrations present in the influent. Therefore, data were not qualified based on the high recoveries. Relative percent differences (RPDs) between the MS and MSD samples were also generally within the acceptance limits.
- For VOCs, LCS/LCSD percent recoveries and RPDs were generally within QAPP acceptance limits. Recoveries of tBA were slightly high and erratic for the Phase 1 sampling event. These observations may indicate a slightly high bias and slightly greater uncertainty associated with the tBA data than for the other critical VOCs. Recoveries of the d<sub>10</sub>-tBA surrogate in the demonstration samples did not show similar bias or imprecision, however.
- Field duplicates were collected and analyzed at a frequency of 5% or more for the two demonstration sampling events. For the Phase 1 event, field duplicate results uniformly met QAPP precision criteria of  $\pm 25\%$  RPD for the critical variables. For the Phase 2 sampling event, RPDs were greater than 25% for tBA in 2 sets of duplicate samples. These samples required dilution due to the presence of other target analytes, however, and the tBA concentrations were near the sample quantitation limits. Therefore, no qualification was added to the data.

Tetra Tech also conducted a cursory quality control review for the non-critical analytical variables. This review was performed to confirm the overall usability of the data in the evaluation of the secondary objectives. Based on this review, the non-critical data were assessed to be usable for their intended uses.

During the first demonstration sampling event, QA supervisory personnel conducted a Technical Systems Audit (TSA) of field sample collection and handling procedures. QA personnel also completed a TSA of the laboratory responsible for analyzing the critical VOC variables (MtBE, tBA, and BTEX). The field TSA also resulted in clarifications and modifications to the sampling procedures established in the QAPP. These generally involved minor changes to documentation practices, sampling schedules, sample containers, and sample identification number formats. In addition, the field TSA increased the frequency of trip blank collection from 5% of the treatment samples to 1 trip blank per cooler of VOC samples. Requirements to collect field blanks and source water blanks were removed.

The laboratory audit noted only one finding. The finding concerned an initial calibration (ICAL) for MtBE that failed to meet relative response factor (RRF) linearity criterion of  $RSD < 15\%$ . The laboratory dropped the 1  $\mu\text{g/L}$  calibration standard from the ICAL curve to meet the relative standard deviation (RSD) criterion, which meant 5  $\mu\text{g/L}$  was then the lowest calibration standard. This was inconsistent with QAPP requirements, and furthermore was technically unacceptable because 5  $\mu\text{g/L}$  was the project treatment goal for MtBE, and it was desirable to accurately quantify MtBE below this level. The QAPP allows the laboratory to use a

linearity criterion of  $r^2 > 0.99$  for the ICAL curve if the RSD criterion is not met. Therefore, as a corrective action, the laboratory added the 1 µg/L standard back into the curve, determined that the  $r^2 > 0.99$  were met, and re-quantified the affected samples.